

**Quality-Assurance Data for Routine Water  
Analyses by the U.S. Geological Survey  
Laboratory in Troy, New York —  
July 1993 through June 1995**



Open-File Report 01-71

U.S. Department of the Interior  
U.S. Geological Survey

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*By* Tricia A. Lincoln, Debra A. Horan-Ross,  
Michael R. McHale, and Gregory B. Lawrence

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Troy, New York  
2001

U.S. DEPARTMENT OF THE INTERIOR

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## ABBREVIATED UNITS OF MEASUREMENT

mg/L	milligrams per liter
µeq/L	microequivalents per liter
µmol/L	micromoles per liter

## Other Abbreviations

ANC	acid-neutralizing capacity
CV	coefficient of variation
DI	deionized water
DQO	data-quality objective
LRTAP	Long-Range Transport of Atmospheric Pollutants
MCV	mean concentration value
MPV	most probable value
QA	quality assurance
QC	quality control
QC-high	high-concentration quality-control sample
QC-low	low-concentration quality-control sample
SRS	Standard Reference Sample
USGS	U.S. Geological Survey

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# Quality-Assurance Data for Routine Water Analyses by the U.S. Geological Survey Laboratory in Troy, New York, July 1993 through June 1995

By Tricia A. Lincoln, Debra A. Horan-Ross, Michael R. McHale, and Gregory B. Lawrence

## Abstract

A laboratory for analysis of low-ionic-strength water has been developed at the U.S. Geological Survey (USGS) office in Troy, N.Y., to analyze samples collected by USGS projects in the Northeast. The laboratory's quality-assurance program is based on internal and interlaboratory quality-assurance samples and quality-control procedures developed to ensure proper sample collection, processing, and analysis. The quality-assurance/quality-control data are stored in the laboratory's SAS<sup>1</sup> data-management system, which provides efficient review, compilation, and plotting of quality-assurance/quality-control data. This report presents and discusses samples analyzed from July 1993 through June 1995.

Quality-control results for 18 analytical procedures were evaluated for bias and precision. Control charts show that data from seven of the analytical procedures were biased throughout the analysis period for either high-concentration or low-concentration samples but were within control limits; these procedures were: acid-neutralizing capacity, dissolved inorganic carbon, dissolved organic carbon (soil expulsions), chloride, magnesium, nitrate (colorimetric method), and pH. Three of the analytical

procedures were occasionally biased but were within control limits; they were: calcium (high for high-concentration samples for May 1995), dissolved organic carbon (high for high-concentration samples from January through September 1994), and fluoride (high in samples for April and June 1994). No quality-control sample has been developed for the organic monomeric aluminum procedure.

Results from the filter-blank and analytical-blank analyses indicate that all analytical procedures in which blanks were run were within control limits, although values for a few blanks were outside the control limits. Blanks were not analyzed for acid-neutralizing capacity, dissolved inorganic carbon, fluoride, nitrate (colorimetric method), or pH.

Sampling and analysis precision are evaluated herein in terms of the coefficient of variation obtained for triplicate samples in 14 of the 18 procedures. Data-quality objectives were met by more than 90 percent of the samples analyzed in all procedures except total monomeric aluminum (85 percent of samples met objectives), total aluminum (70 percent of samples met objectives), and dissolved organic carbon (85 percent of samples met objectives). Triplicate samples were not analyzed for ammonium, fluoride, dissolved inorganic carbon, or nitrate (colorimetric method).

Results of the USGS interlaboratory Standard Reference Sample Program indicated high data quality with a median result of 3.6 of a possible

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4.0. Environment Canada's LRTAP interlaboratory study results indicated that more than 85 percent of the samples met data-quality objectives in 6 of the 12 analyses; exceptions were calcium, dissolved organic carbon, chloride, pH, potassium, and sodium. Data-quality objectives were not met for calcium samples in one LRTAP study, but 94 percent of samples analyzed were within control limits for the remaining studies. Data-quality objectives were not met by 35 percent of samples analyzed for dissolved organic carbon, but 94 percent of sample values were within 20 percent of the most probable value. Data-quality objectives were not met for 30 percent of samples analyzed for chloride, but 90 percent of sample values were within 20 percent of the most probable value. Measurements of samples with a pH above 6.0 were biased high in 54 percent of the samples, although 85 percent of the samples met data-quality objectives for pH measurements below 6.0. Data-quality objectives for potassium and sodium were not met in one study (only 33 percent of the samples analyzed met the objectives), although 85 percent of the sample values were within control limits for the other studies. Measured sodium values were above the upper control limit in all studies.

Results from blind reference-sample analyses indicated that data-quality objectives were met by more than 80 percent of the chloride, pH, potassium, and sodium samples. Data-quality objectives were not met by 35 percent of the magnesium samples and 45 percent of the sulfate samples. Data-quality objectives were not met by calcium samples.

## INTRODUCTION

The U.S. Geological Survey (USGS) maintains a laboratory at its Troy, N.Y., office to analyze low-ionic-strength water for USGS watershed-research projects that require major-ion analyses of precipitation, soil-water, shallow ground-water, and stream-water samples. The methods used in this laboratory are described in detail in Lawrence and others (1995).

Analyses done during the 2-year period (July 1993-June 1995) represented by this report were: acid-neutralizing capacity (ANC), total monomeric aluminum, organic monomeric aluminum, total aluminum, ammonium, calcium, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), chloride, fluoride, magnesium, nitrate (ion chromatograph and colorimetric method), pH, potassium, silicon, sodium, and sulfate.

## Purpose and Scope

This report documents the quality-assurance practices and quality-control data of this laboratory and is intended for use by current and prospective cooperating agencies. It (1) describes quality-control and quality-assurance procedures of the laboratory, (2) presents graphs showing the results from analyses of quality-control samples, filter blanks and analytical blanks, triplicate environmental samples, and blind reference samples, and (3) explains analytical biases and outliers and the corrective actions taken.

## Participating Projects

The numbers and types of samples analyzed by the laboratory during the 2-year period are summarized below, by the project for which they are associated; numbers in parentheses are USGS project numbers.

**Project:** Neversink Watershed Study (NY91-200)

**Cooperator:** New York City Department of Environmental Protection

**Analyses:** 997 samples (stream water, shallow ground water, and snow).

**Project:** Biogeochemical Processes that Control Nitrogen Cycling and Associated Hydrogen and Aluminum Leaching in an Undeveloped Headwater Basin (NY91-204)

**Cooperator:** New York City Department of Environmental Protection

**Analyses:** 3,100 samples (stream water, shallow ground-water, soil water solution, soil water by expulsion method, and snow).

**Project:** Long-Term Monitoring of Five Streams in the Catskill Mountains (NY85-152)

**Cooperator:** U.S. Environmental Protection Agency

**Analyses:** 370 stream-water samples.

**Project:** Forest-Floor Aluminum and Calcium Chemistry—Relations with Acid Deposition, Root Vitality, Stand Dynamics, and Red Spruce (NY92-208)

**Cooperator:** U.S. Forest Service

**Analyses:** 360 samples (stream water, soil water solution, and soil water by expulsion method).

**Project:** Variable Source-Area Control of Episodic Stream Chemistry (NY92-209)

**Cooperator:** U.S. Forest Service

**Analyses:** 348 stream-water samples.

Additional information on projects of the New York District is given in Lee (1996).

## **QUALITY-ASSURANCE/QUALITY-CONTROL (QA/QC) PROGRAM DESCRIPTION**

The quality of the data produced at this laboratory is maintained by adherence to the standard operating procedures described in Lawrence and others (1995) and by participation in externally administered quality-assurance (QA) programs. Results of QA data are evaluated by the laboratory supervisor and primary analysts, and appropriate corrective action is taken when needed. The data quality objectives (DQO's) are based on (1) the precision and accuracy levels generally required in projects using the Troy Laboratory, and (2) the analytical limits of the methods used.

### **Quality-Control Samples**

Quality-control (QC) samples are used to determine the accuracy of an instrument's calibration and to detect variations in instrument response within an analytical run. Source material for all QC samples either is obtained from a manufacturer other than the producer of the source material used to make calibration standards, or is obtained from a different lot.

The concentrations of QC samples are chosen to bracket the expected range of the environmental-sample concentrations. A high-concentration QC sample and a low-concentration QC sample (referred to herein as QC-high and QC-low) are prepared for most analyses; exceptions are inorganic monomeric aluminum, for which column efficiency is used to

determine the acceptability of the data, and fluoride, for which only one QC sample is prepared because the concentrations encountered by the laboratory are within a narrow range.

Quality-control samples are analyzed immediately after calibration, after every 10 analyses of environmental samples, and at the end of each run. Exceptions to the frequency of QC-sample analyses are ANC (after every 17 environmental samples), and pH (after every 10 to 13 environmental samples). QC samples that do not meet DQO's for accuracy are rerun, and if the value is acceptable, the run is continued. If the rerun-QC-sample value is unacceptable, the environmental-sample data preceding it are rejected, and the instrument is recalibrated. Only accepted QC-sample and environmental-sample data are entered into the database. An exception to this practice occurs when the volume of an environmental sample is insufficient for a rerun. In this case, the environmental-sample and QC data are entered into the database and flagged, and the project chief then decides whether to accept or reject these data. Analytical results of QC samples are included in this report to indicate (1) the frequency of out-of-control data that are not rerun, and (2) biases and trends of within control data. The number of samples analyzed, and a summary of the quality-assurance data, are given in table 1.

### **Filter Blanks and Analytical Blanks**

A filter blank and an analytical blank are included in each group of 50 environmental samples.

*Filter blanks* are aliquots of deionized (DI) water that are processed and analyzed in the same manner as environmental samples. Filter blanks are analyzed only for constituents that require filtration. Filter-blank analysis indicates whether contamination has occurred during bottle-washing procedures, filtration, sample preservation, or laboratory analysis.

*Analytical blanks* are aliquots of DI water that are processed and analyzed as environmental samples, except that the filtration step is omitted. Contamination found in analytical blanks may be attributed to bottle washing, sample preservation, or laboratory analysis, but not to filtration.

**Table 1.** Number of environmental and quality-control samples analyzed by USGS Laboratory, and summary of quality-control (QC) data for each constituent, July 1993 through June 1995.

[QC-high = high concentration quality-control sample. QC-low = low concentration quality-control sample.]

Constituent	Summary of QC data						
	Number of samples analyzed			Number of QC samples exceeding control limits		Number of QC samples exceeding control limits by more than 5 percent	
	Project samples	QC samples QC-high	QC-low	QC-high	QC-low	QC-high	QC-low
Acid-neutralizing capacity	3713	68	307	0	0	0	0
Aluminum, total monomeric	4038	564	564	1	2	0	1
Aluminum, organic monomeric	4038	0	0	0	0	0	0
Aluminum, total	4594	730	736	11	7	4	5
Ammonium	1381	394	394	7	7	0	1
Calcium	5707	509	509	2	7	0	1
Carbon, dissolved inorganic	289	68	68	1	1	0	0
Carbon, dissolved organic	4204	560	561	0	14	0	5
Carbon, dissolved organic (soil expulsions)	352	33	33	0	3	0	0
Chloride	4186	589	589	0	0	0	0
Fluoride	2041	405	0	1	0	1	0
Magnesium	4304	514	514	5	2	2	0
Nitrate (ion chromatography)	4450	602	603	0	1	0	0
Nitrate (colorimetric method)	976	195	195	2	1	0	0
pH	4124	115	507	1	2	0	1
Potassium	3745	437	437	1	6	1	2
Silicon	4175	615	615	6	3	0	0
Sodium	3750	444	444	1	4	0	0
Sulfate	4171	586	586	0	0	0	0

### Triplicate Environmental Samples

One set of field triplicate environmental samples is included in each group of 50 samples. A field triplicate set consists of three consecutive samples taken from one site. The purpose of environmental triplicate samples is to determine long-term analytical precision. Precision can be affected by bottle washing, sample-collection, sample processing procedures, and analysis. Environmental samples are selected for triplicate analysis on a rotating basis to ensure a wide range of sample concentrations.

Triplicate environmental samples were analyzed consecutively on the instrument sample tray until

December 1993. Presently, the laboratory alternates between consecutively analyzing a triplicate set and separating the triplicate set over the day's analysis run.

### U.S. Geological Survey's Standard Reference Sample Program

The USGS Standard Reference Sample Program (SRS) conducts a national interlaboratory analytical evaluation program semiannually. The Troy laboratory participates in the low-ionic-strength component of this program. Reference samples are prefixed by a P and are analyzed for calcium, chloride, fluoride,

magnesium, pH, potassium, sodium, and sulfate. Typically, the low-ionic-strength sample consists of snow that is collected, melted, filtered, and possibly spiked with reagent-grade chemicals to meet the goals of the SRS program. Laboratory personnel are aware of the presence of the SRS sample at the time of analysis but do not know the constituent concentrations until a published report is received from the USGS. The most probable value (MPV) for each constituent is calculated by nonparametric statistics. Individual laboratory performances are rated numerically; the highest score is 4.0, and the lowest is 0.0.

### **Environment Canada's LRTAP Interlaboratory Study**

The Troy laboratory participates in the LRTAP interlaboratory quality-assurance program, in which a set of 10 samples is analyzed three times per year. The samples are obtained from predominantly low-ionic-strength waters from various sources, such as precipitation, snow, lakes, and streams throughout North America and western Europe. The concentrations of the constituents in the LRTAP samples are similar to those of the environmental samples analyzed at the Troy laboratory. Laboratory results are compared with a median concentration value (MCV) calculated from results from all participants in the LRTAP program. Laboratory personnel are aware of the presence of LRTAP samples at the time of analysis but do not know the MCV of the constituents until Environment Canada publishes a report at the conclusion of each study.

### **Blind Reference Samples**

The Troy laboratory analyzes USGS SRS samples that have been processed as routine environmental samples. These blind reference samples are disguised and therefore assumed by the analyst to be a project sample. The blind reference samples have most probable values that are reported by the USGS SRS program. The SRS samples are rotated as supplies are exhausted, and periodically the identity of the blind reference sample is changed. One blind reference sample is included in each set of 50 environmental samples.

## **CONTROL-CHART DEVELOPMENT AND EVALUATION**

Control charts (figs. 1-5) are plots of QC data in relation to time; in this report, they are used to (1) confirm that laboratory DQO's are met for individual QC samples, (2) detect long-term biases within the control limits, and (3) provide comparisons with results from other laboratories.

A constituent analysis is considered biased if 70 percent or more of the points on a chart are above or below the theoretical value.

### **Quality-Control Samples**

Results of QC sample analyses are plotted on control charts in which the central line is equal to the theoretical value of the control sample. Each analyte has prescribed control limits that have been established to meet project DQO's (table 2). The limits are represented by the upper and lower control-limit lines on each chart. QC-high and QC-low samples are plotted on separate graphs by constituent and date of analysis, and the control charts are evaluated for trends and(or) bias. All data are reported in micromoles per liter ( $\mu\text{mol/L}$ ) except pH (pH units) and ANC (microequivalents per liter,  $\mu\text{eq/L}$ ).

During the period represented by this report, several quality-control samples concentrations were changed to reflect typical environmental-sample concentrations (for example, fig. 1M). The concentration changes are discussed in the summary of results.

### **Filter Blanks and Analytical Blanks**

Results from blank analyses (fig. 2) are plotted on control charts, by constituent. The control limits were established to meet project DQO's (table 2) and are represented by horizontal lines on the control charts. Data are plotted as concentration in relation to date of collection. The control charts are evaluated to identify possible contamination or positive interferences.

### **Triplicate Environmental Samples**

The coefficient of variation (CV) for each triplicate sample concentration is plotted by constituent and date of collection in figure 3. Data

**Table 2.** Reporting limits and data-quality objectives for accuracy, precision, and blanks for solution analyses performed by the U.S. Geological Survey Laboratory in Troy, N.Y., July 1993 through June 1995.

[DQO, data-quality objective,  $\mu\text{mol/L}$ , micromoles per liter. CV, coefficient of variation. ANC, acid-neutralizing capacity. pH and ANC values (in parentheses) are in pH units and microequivalents per liter, respectively.]

Constituent or property	Reporting limit ( $\mu\text{mol/L}$ )	Accuracy				Precision	
		Low-concentration quality-control sample		High-concentration quality-control sample		DQO (CV)	Filter and analytical blanks DQO ( $\mu\text{mol/L}$ )
		DQO (percent error)	Concentration ( $\mu\text{mol/L}$ )	DQO (percent error)	Concentration ( $\mu\text{mol/L}$ )		
Acid-neutralizing capacity <sup>1</sup>	none	10	(-39.9)	10	(125)	10	none
Aluminum, total monomeric	1.5	15	7.41	10	18.5	15	0.75
Aluminum, organic monomeric <sup>2</sup>	1.5	none	none	none	none	15	0.75
Aluminum, total	1.0	20	1.0	10	15.0	10	0.5
Ammonium	2.0	15	7.14	10	17.9	10	1.0
Calcium	2.0	10	25.0	10	99.8	10	1.0
Carbon, dissolved inorganic <sup>3</sup>	41.0	15	83.3	10	416	10	none
Carbon, dissolved organic <sup>3</sup>	41.0	15	83.3	10	416	10	18
Carbon, dissolved organic (soil expulsions) <sup>3</sup>	41.0	10	416	10	1665	10	none
Chloride	2.0	10	8.47	10	84.7	10	0.5
Fluoride	0.5	15	1.58	none	none	10	none
Magnesium	1.0	10	8.23	10	32.9	10	0.5
Nitrate (ion chromatography)	2.0	10	4.84	10	48.4	10	0.3
Nitrate (colorimetric method)	5.0	15	42.9	10	100	10	none
pH <sup>4</sup>	none	10	(4.41)	20	(6.88)	10	none
Potassium	1.0	10	5.12	10	25.6	10	0.5
Silicon	6.0	10	35.6	10	107	10	3
Sodium	1.0	10	8.70	10	43.5	10	1.0
Sulfate	2.0	10	8.33	10	83.3	10	0.3

<sup>1</sup> ANC: Values in parentheses are in microequivalents per liter. For values within  $\pm 20$  microequivalents per liter, an absolute data-quality objective of  $\pm 6$  microequivalents per liter is used for precision.

<sup>2</sup> Quality-control samples for organic monomeric aluminum are unavailable.

<sup>3</sup> Concentrations are expressed as micromoles carbon per liter.

<sup>4</sup> pH: Percent error and coefficient of variation determined from  $[\text{H}^+]$ .

with mean concentrations less than the defined reporting limit (table 2) are excluded. The DQO for all constituents is a CV of less than 10 percent, with the exception of total monomeric aluminum and organic monomeric aluminum, which are 15 percent. Each circle within the control charts represents the CV of a triplicate environmental sample.

$$CV = \frac{s}{\bar{x}}(100)$$

where:  $s$  = standard deviation, and

$\bar{x}$  = arithmetic mean of triplicate samples

ANC triplicate sample means were plotted on two graphs. The first graph shows the CV for triplicate sample means outside the range of -20 to +20  $\mu\text{eq/L}$  (fig. 3A1); the second graph shows values that fall

between -20 and +20 µeq/L (fig. 3A2). Each symbol on the graph represents the difference between the triplicate sample mean and the individual values of that triplicate sample.

## Environment Canada's LRTAP Interlaboratory Study

Interlaboratory comparison graphs (fig. 4) are based on results from LRTAP samples and represent LRTAP studies from July 1993 through March 1995. The Troy laboratory did not participate in Study 34 (October 1993). Samples with MCV's less than the reporting limits were excluded from the graphs. The MCV and the control limits of ±10 percent are represented by lines on the graphs; the percent difference (*D*) is calculated as:

$$D = [(AV - MCV)/MCV] \times 100$$

where: AV = analyzed value, and

MCV = mean concentration value

A separate graph is shown for ANC values in the +20 to -20 µeq/L range; results for these samples are plotted as the difference between the laboratory value and the MCV (fig. 4A2). The LRTAP pH results consist of two sets of data—pH values less than 6.00, and pH values equal to or greater than 6.00. The two sets of data have different DQO's, which are represented by a solid line and a dashed line on the pH graph (fig. 4H).

## Blind Reference Samples

Results from blind reference sample analyses (fig.5) are plotted on separate control charts, by constituent and date of analysis. Samples with MPV's less than the reporting limits were excluded from the graphs. The MPV and the control limits of ±10 percent are represented by lines on the graphs; the percent difference (*D*) is calculated as:

$$D = [(AV - MPV)/MPV] \times 100$$

where: AV = analyzed value, and

MPV = most probable value

## SUMMARY OF RESULTS

The following sections summarize the results for (A) quality-control samples (fig. 1, p. 14-18), (B) filter blanks and analytical blanks (fig 2, p.19-20), (C) triplicate environmental samples (fig. 3, p. 21-22), (D) SRS samples (table 3), (E) LRTAP samples (fig. 4, p. 23-24), and (F) blind samples (fig. 5, p. 25).

### A. Quality-Control Samples

**Acid-Neutralizing Capacity** (fig. 1A).—DQO's were met by 100 percent of the samples. No apparent trends or biases were evident among the QC-low sample. The QC-high sample had a low bias during this time period.

**Aluminum, Total Monomeric** (fig. 1B).—DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples.

**Aluminum, Organic Monomeric**.—No QC sample has been developed for this analysis.

**Aluminum, Total** (fig. 1C).—DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples.

**Ammonium** (fig. 1D).—DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples.

**Calcium** (fig. 1E).—DQO's were met by 99 percent of the samples. A slight high bias was observed for analyses performed in May 1995.

**Carbon, Dissolved Inorganic** (fig. 1F).—DQO's were met by 99 percent of the samples. The QC-high and QC-low samples were biased high during this time period.

**Carbon, Dissolved Organic** (fig. 1G).—DQO's were met by 99 percent of the samples. A high bias was observed for the QC-high sample in 1994. No apparent trend or bias was evident for the QC-low sample.

**Carbon, Dissolved Organic (soil expulsions)** (fig. 1H).—DQO's were met by 95 percent of the

samples. The QC-high graph shows a slight high bias.

**Chloride** (fig. 1I).—DQO's were met by 100 percent of the samples. The QC-high graph illustrates a low bias until December 1993; this was due to an error in preparation of QC stock solution and has been corrected. The QC-low sample shows a possible high bias which has been corrected by adding a blank standard to the calibration curve. Data was flagged in the database.

**Fluoride** (fig. 1J).—DQO's were met by 99 percent of the samples. The high bias in early 1994 is attributed to the QC stock solution, which was replaced.

**Magnesium** (fig. 1K).—DQO's were met by 99 percent of the samples. The QC-high and QC-low samples appear to have a slight low bias.

**Nitrate (ion chromatography)** (fig. 1L).—DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples.

**Nitrate (colorimetric method)** (fig. 1M).—DQO's were met by 99 percent of the samples. The QC-high and QC-low samples appear to be biased low; this is attributed to incomplete conversion of nitrate to nitrite by the cadmium-reduction column. The column was operating at 90-percent efficiency during this period. Project chiefs were notified of the low bias; data were not changed. In July 1994, the QC-high and QC-low concentrations were changed to 99.99 and 42.88  $\mu\text{mol/L}$ , respectively, to reflect typical environmental-sample concentrations.

**pH** (fig. 1N).—DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-high sample. The QC-low sample had a high bias during this time period.

**Potassium** (fig. 1O).—DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples. The potassium QC-low concentration was increased from 5.12 to 6.40  $\mu\text{mol/L}$  in 1995 to reflect typical environmental-sample concentrations.

**Silicon** (fig. 1P).—DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among QC-low samples. The QC-high sample had a slight high bias during this time period. The QC-low control limit was lowered to 10 percent in response to the improvement and refinement of the analysis.

**Sodium** (fig. 1Q).—DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples. The sodium QC-low concentration was increased from a theoretical value of 8.70 to 10.88  $\mu\text{mol/L}$  in 1995 to reflect typical environmental-sample concentrations.

**Sulfate** (fig. 1R).—DQO's were met by 100 percent of the samples. No apparent trends or biases were evident among the QC-high sample. The QC-low sample had a slight high bias during this time period.

## B. Filter Blanks and Analytical Blanks

**Acid-Neutralizing Capacity**.—Blanks were not analyzed for this constituent.

**Aluminum, Total Monomeric** (fig. 2A).—The DQO was met by 93 percent of the samples. High blank results were obtained in July and August of 1993. The instrument software, which calculates sample-analysis results, was upgraded, and an incorrect default setting was discovered that subtracted the absorbance of the leading baseline from the sample peak absorbance. This has been corrected; the software now calculates an average absorbance from the leading and trailing baselines and subtracts this value from the sample peak. Sample data were flagged in the database.

**Aluminum, Organic Monomeric** (fig. 2B).—The DQO was met by 94 percent of the samples. High blank results were obtained in July and August of 1993. The instrument software, which calculates sample-analysis results, was upgraded, and an incorrect default setting was discovered that subtracted the absorbance of the leading baseline from the sample peak absorbance. This has been corrected; the software now calculates an average absorbance from the leading and trailing baselines and subtracts this value from the sample peak. Sample data was flagged in the database.

**Aluminum, Total** (fig. 2C).—The DQO was met by 79 percent of the samples. No systematic trends were evident for this analysis.

**Ammonium** (fig. 2D).—The DQO was met by 93 percent of the samples. No systematic trends were evident for this analysis. Routine blanks were discontinued for the ammonium analysis in October of 1993. Ammonium was not analyzed for

every environmental sample after this date.

Samples were frozen and then analyzed in batches throughout the year.

**Calcium** (fig. 2E).—The DQO was met by 91 percent of the samples. No systematic trends were evident for this analysis.

**Carbon Dissolved Inorganic**.—Blanks were not analyzed for this constituent.

**Carbon, Dissolved Organic** (fig. 2F).—The DQO was met by 84 percent of the samples. A new instrument has been purchased, which is expected to increase the percent of samples that met the DQO.

**Carbon, Dissolved Organic (soil expulsions)**.—Blanks were not analyzed for this constituent.

**Chloride** (fig. 2G).—The DQO was met by 80 percent of the samples.

**Fluoride**.—Blanks were not analyzed for this constituent.

**Magnesium** (fig. 2H).—The DQO was met by 96 percent of the samples. No systematic trends were evident for this analysis.

**Nitrate (ion chromatography)** (fig. 2I).—The DQO was met by 93 percent of the samples. No systematic trends were evident for this analysis.

**Nitrate (colorimetric method)**.—Blanks were not analyzed for this constituent.

**pH**.—Blanks were not analyzed for this constituent.

**Potassium** (fig. 2J).—The DQO was met by 88 percent of the samples. No systematic trends were evident for this analysis.

**Silicon** (fig. 2K).—The DQO was met by 78 percent of the samples. No systematic trends were evident for this analysis.

**Sodium** (fig. 2L).—The DQO was met by 90 percent of the samples. No systematic trends were evident for this analysis.

**Sulfate** (fig. 2M).—The DQO was met by 97 percent of the samples. No systematic trends were evident for this analysis.

### C. Triplicate Environmental Samples

**Acid-Neutralizing Capacity** (figs. 3A1 and 3A2).—The DQO was met by 96 percent of the triplicate samples.

**Aluminum, Total Monomeric** (fig. 3B).—The DQO was met by 78 percent of the triplicate samples.

**Aluminum, Organic Monomeric** (fig. 3C).—The DQO was met by 93 percent of the triplicate samples.

**Aluminum, Total** (fig. 3D).—The established precision DQO was exceeded by 42 percent of the samples. Use of a graphite furnace for aluminum analysis has been discontinued. An ICP has been purchased, and improved results are expected.

**Ammonium**.—Triplicate samples were not analyzed for ammonium.

**Calcium** (fig. 3E).—The DQO was met by 91 percent of the triplicate samples.

**Carbon Dissolved Inorganic**.—Triplicate samples were not analyzed for ammonium.

**Carbon, Dissolved Organic** (fig. 3F).—The DQO was met by 82 percent of the triplicate samples.

**Carbon, Dissolved Organic (soil expulsions)**.—Triplicate samples were not analyzed for ammonium.

**Chloride** (fig. 3G).—The DQO was met by 89 percent of the triplicate samples.

**Fluoride**.—Triplicate samples were not analyzed for ammonium.

**Magnesium** (fig. 3H).—The DQO was met by 98 percent of the triplicate samples.

**Nitrate (ion chromatography)** (fig. 3I).—The DQO was met by 89 percent of the triplicate samples.

**Nitrate (colorimetric method)**.—Triplicate samples were not analyzed for ammonium.

**pH** (fig. 3J).—The DQO was met by 100 percent of the triplicate samples.

**Potassium** (fig. 3K).—The DQO was met by 89 percent of the triplicate samples.

**Silicon** (fig. 3L).—The DQO was met by 97 percent of the triplicate samples.

**Sodium** (fig. 3M).—The DQO was met by 92 percent of the triplicate samples.

**Sulfate** (fig. 3N).—The DQO was met by 100 percent of the triplicate samples.

**D. U.S. Geological Survey's Standard Reference Sample (SRS) Program**

Laboratory results for all SRS samples were rated between "good" and "excellent." Overall laboratory performance ratings for each SRS sample were:

P-21 4.0  
P-22 3.7  
P-23 3.4  
P-24 3.3

All analyses received a rating of 3 or 4 for each constituent with two exceptions. pH received a 2 rating for P-22 but improved to 4 in both samples that followed. Sodium received a 2 for P-23.

**Table 3.** Results obtained by Troy, N.Y., Laboratory for U.S. Geological Survey Standard Reference Sample (SRS) Program, October 1993 through May 1995

(MPV, most probable value; TV, Troy laboratory value; mg/L, milligrams per liter; dash indicates no results reported)

Analyte	MPV, TV, and rating <sup>a</sup>	SRS sample number			
		P-21 10/93 <sup>b</sup>	P-22 4/94 <sup>c</sup>	P-23 10/94 <sup>d</sup>	P-24 5/95 <sup>e</sup>
Calcium	MPV, mg/L	—	0.725	1.13	—
	TV, mg/L	—	0.760	1.20	—
	Rating	—	3	3	—
Chloride	MPV, mg/L	3.90	2.92	0.310	1.20
	TV, mg/L	3.83	2.90	0.205	1.10
	Rating	4	4	3	3
Fluoride	MPV, mg/L	—	0.028	0.120	—
	TV, mg/L	—	0.020	0.120	—
	Rating	—	4	4	—
Magnesium	MPV, mg/L	—	0.098	0.317	—
	TV, mg/L	—	0.100	0.320	—
	Rating	—	4	4	—
pH	MPV	4.06	5.81	6.40	4.73
	TV	4.06	5.60	6.33	4.72
	Rating	4	2	4	4
Potassium	MPV, mg/L	—	0.203	0.483	—
	TV, mg/L	—	0.210	0.450	—
	Rating	—	4	3	—
Sodium	MPV, mg/L	—	1.70	0.500	—
	TV, mg/L	—	1.70	0.420	—
	Rating	—	4	2	—
Sulfate	MPV, mg/L	0.50	0.728	1.28	0.338
	TV, mg/L	0.46	0.785	1.27	0.335
	Rating	4	4	4	4

- <sup>a</sup> Laboratory rating system: 4 is highest score; 0 is lowest
- <sup>b</sup> Sample described in Long and Farrar (1994a)
- <sup>c</sup> Sample described in Long and Farrar (1994b)
- <sup>d</sup> Sample described in Long and Farrar (1995a)
- <sup>e</sup> Sample described in Long and Farrar (1995b)

## E. Environment Canada's LRTAP Interlaboratory Study

Environment Canada's LRTAP program does not audit the analysis of total monomeric aluminum, organic monomeric aluminum, dissolved inorganic carbon, dissolved organic carbon (soil expulsions), fluoride, and nitrate (colorimetric method).

The laboratory did not submit results for total aluminum analyses during this time period.

**Acid-Neutralizing Capacity** (figs. 4A1 and 4A2).—The DQO was met by 98 percent of the LRTAP samples. No trend or bias was evident.

**Ammonium** (fig. 4B).—The DQO was met by 100 percent of the LRTAP samples. LRTAP samples were not run for ammonium after study 33. Environmental samples are no longer routinely analyzed for ammonium. Samples are selectively analyzed a few times yearly.

**Calcium** (fig. 4C).—The DQO was met by 76 percent of the LRTAP samples. The low bias in study 38 was due to incorrect dilutions of stock solutions.

**Carbon, Dissolved Organic** (fig. 4D).—The DQO was met by 70 percent of the LRTAP samples. The outliers were most often biased low.

**Chloride** (fig. 4E).—The DQO was met by 76 percent of the LRTAP samples. All outliers were biased high.

**Magnesium** (fig. 4F).—The DQO was met by 88 percent of the LRTAP samples. No trend or bias was evident.

**Nitrate** (ion chromatography).—The DQO was met by 97 percent of the LRTAP samples.

**pH** (fig. 4H).—The DQO was met by 85 percent of the LRTAP samples with a pH less than 6.00. Samples with a pH above 6.00 were biased high. The high number of pH measurements that were biased high are most likely the result of a difference in methods used by the Troy laboratory and the other laboratories participating in the LRTAP program. The USGS method uses a millivolt-stability criterion to determine whether equilibration with the electrode has occurred. Most laboratories use a preset time for all samples. Low-pH samples equilibrate more quickly than high-pH samples. Laboratories that use the same equilibration time for low and high pH samples will, therefore, bias their measurement of a high-pH sample if this sample is preceded by a low-pH sample. This relation explains why about half of the LRTAP pH measurements appear to be biased high. Successful

measurement of the pH of quality-control samples with values above 6.7 supports this conclusion.

**Potassium** (fig. 4I).—The DQO was met by 66 percent of the LRTAP samples. All outliers were biased low.

**Silicon** (fig. 4J).—The DQO for silicon was not met. All data was biased high. An ICP was recently installed for silicon analysis, and improved results are expected.

**Sodium** (fig. 4K).—The DQO was met by 66 percent of the LRTAP samples. The low percentage was primarily the result of a low bias in all samples from study 35. The cause is uncertain, but 80 percent of the samples since that study have met the DQO's.

**Sulfate** (fig. 4L).—The DQO was met by 98 percent of the samples. No trend or bias was evident.

## F. Blind Reference Samples

Blind reference samples are analyzed for all constituents for which the SRS program reports. The blind reference samples are not analyzed for acid-neutralizing capacity, total monomeric aluminum, organic monomeric aluminum, total aluminum, ammonium, dissolved inorganic carbon, dissolved organic carbon, dissolved organic carbon (soil expulsions), fluoride, nitrate (ion chromatography), nitrate (colorimetric method), and silicon.

**Calcium** (fig. 5A).—The DQO for calcium was not met. The calcium method used during this period included a lanthanum chloride reagent, whose concentration was too low to mask interferences. Environmental-sample data were erroneously low. The method was corrected, and project samples were reanalyzed for calcium. Initial data were flagged as erroneous, and reanalysis data were added to the database.

**Chloride** (fig. 5B).—The DQO was met by 91 percent of the blind reference samples. No trend or bias was evident.

**Magnesium** (fig. 5C).—The DQO was met by 59 percent of the blind reference samples.

**pH** (fig. 5D).—The DQO was met by 100 percent of the blind reference samples. No trend or bias was evident.

**Potassium** (fig. 5E).—The DQO was met by 77 percent of the blind reference samples. No trend or bias was evident.

**Sodium** (fig. 5F).—The DQO was met by 80 percent of the blind reference samples. Most of the outliers were biased low.

**Sulfate** (fig. 5G).—The DQO was met by 51 percent of the samples. All outliers were biased low. The SRS sample that was used as the blind reference sample during this period was 8 years old. The sulfate MPV's may have been inaccurate after this long time period. More recent SRS samples are currently used for blind reference samples, and results have improved.

## SELECTED REFERENCES

- Lawrence, G.B., Lincoln, T.A., Horan-Ross, D.A., Olson, M.L., and Waldron, L.A., 1995, Analytical methods of the U.S. Geological Survey's New York District Water Analysis Laboratory: U.S. Geological Survey Open-File Report 95-416, 78 p.
- Lee, M.P., 1996, U.S. Geological Survey Water-Resources Programs in the New York District—fiscal years 1993-94: U.S. Geological Survey Open-File Report 96-113, 48 p.
- Long, H. K., and Farrar, J. W., 1994a, Report on the U.S. Geological Survey's evaluation program for Standard

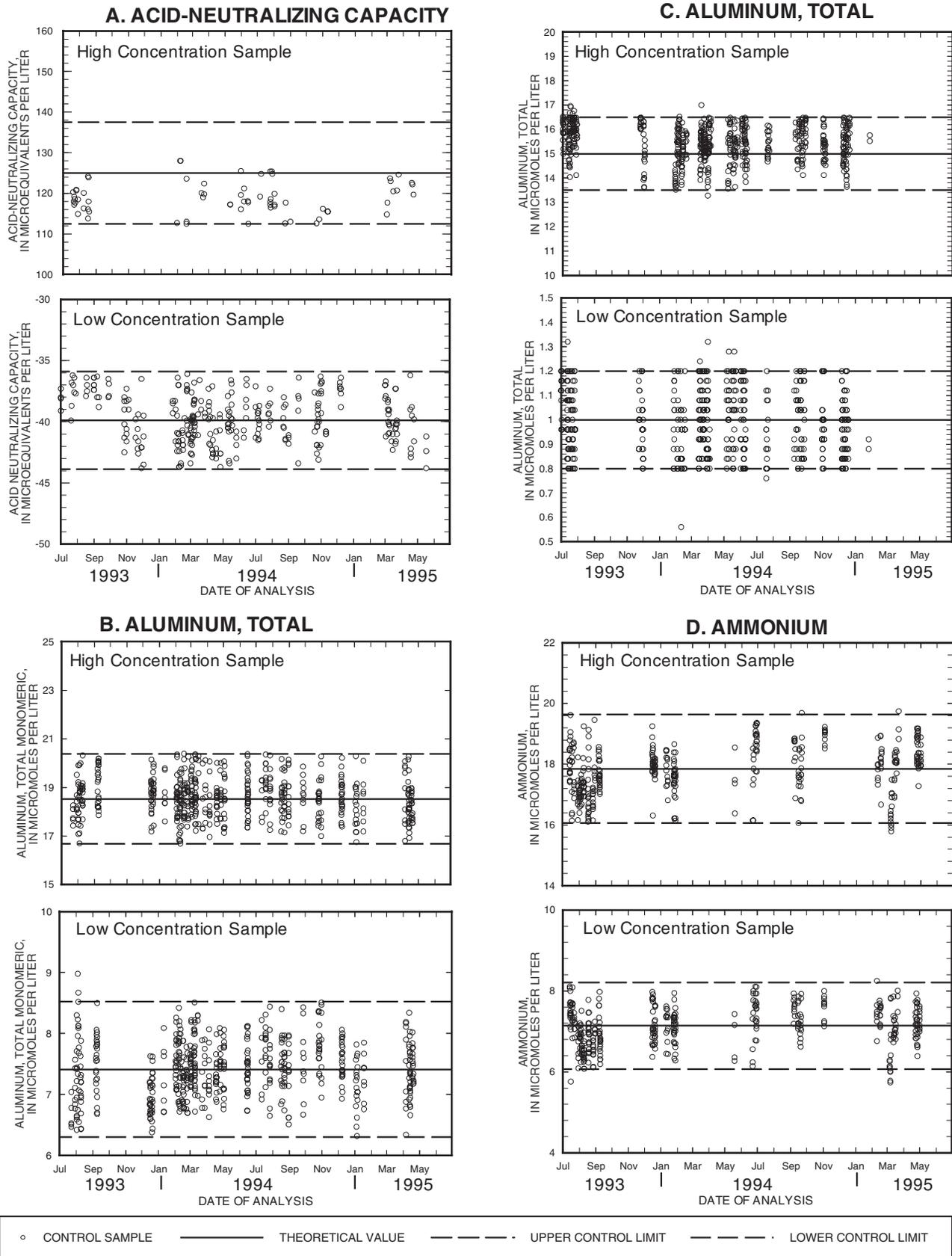
Reference Samples distributed in October 1993 T-127 (trace constituents), M-128 (major constituents), N-40 (nutrients), N-41 (nutrients), P-21 (low ionic strength), and Hg-17 (mercury), AMW-3 (acid mine water), and WW-1 (whole water): U.S. Geological Survey Open-File Report 94-42, 177 p.

\_\_\_\_\_, 1994b, Report on the U.S. Geological Survey's evaluation program for Standard Reference Samples distributed in April 1994: T-129 (trace constituents), M-130 (major constituents), N-42 (nutrients), P-22 (low ionic strength), and Hg-18 (mercury): U.S. Geological Survey Open-File Report 94-369, 101 p.

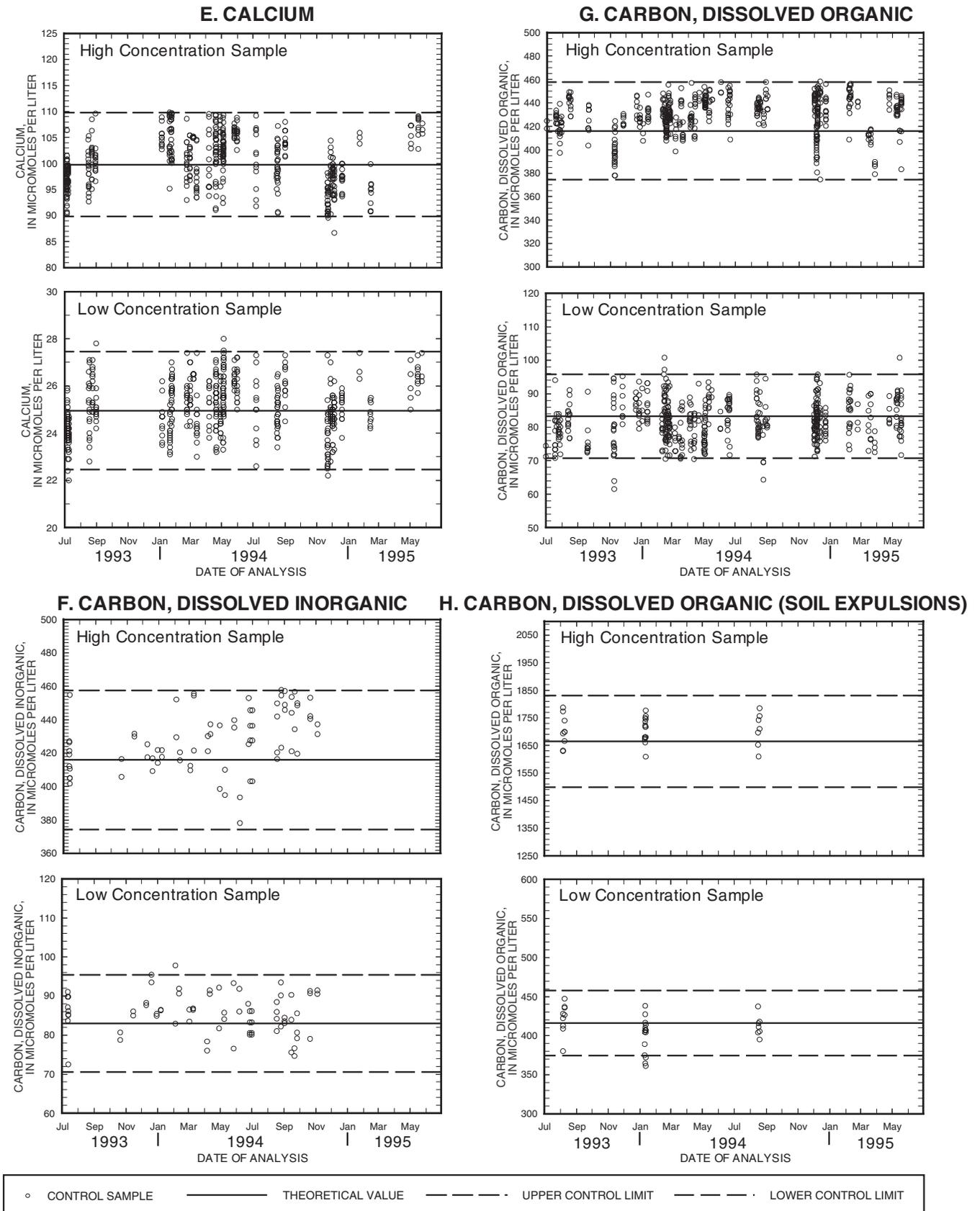
\_\_\_\_\_, 1995a, Report on the U.S. Geological Survey's evaluation program for Standard Reference Samples distributed in October 1994: T-131 (trace constituents), T-133 (trace constituents), M-132 (major constituents), N-43 (nutrients), N-44 (nutrients), P-23 (low ionic strength), and Hg-19 (mercury): U.S. Geological Survey Open-File Report 95-117, 139 p.

\_\_\_\_\_, 1995b, Report on the U.S. Geological Survey's evaluation program for Standard Reference Samples distributed in May 1995: T-135 (trace constituents), M-134 (major constituents), N-45 (nutrients), N-46 (nutrients), P-24 (low ionic strength), Hg-20 (mercury), and SED-5 (bed material): U.S. Geological Survey Open-File Report 95-395, 135 p.

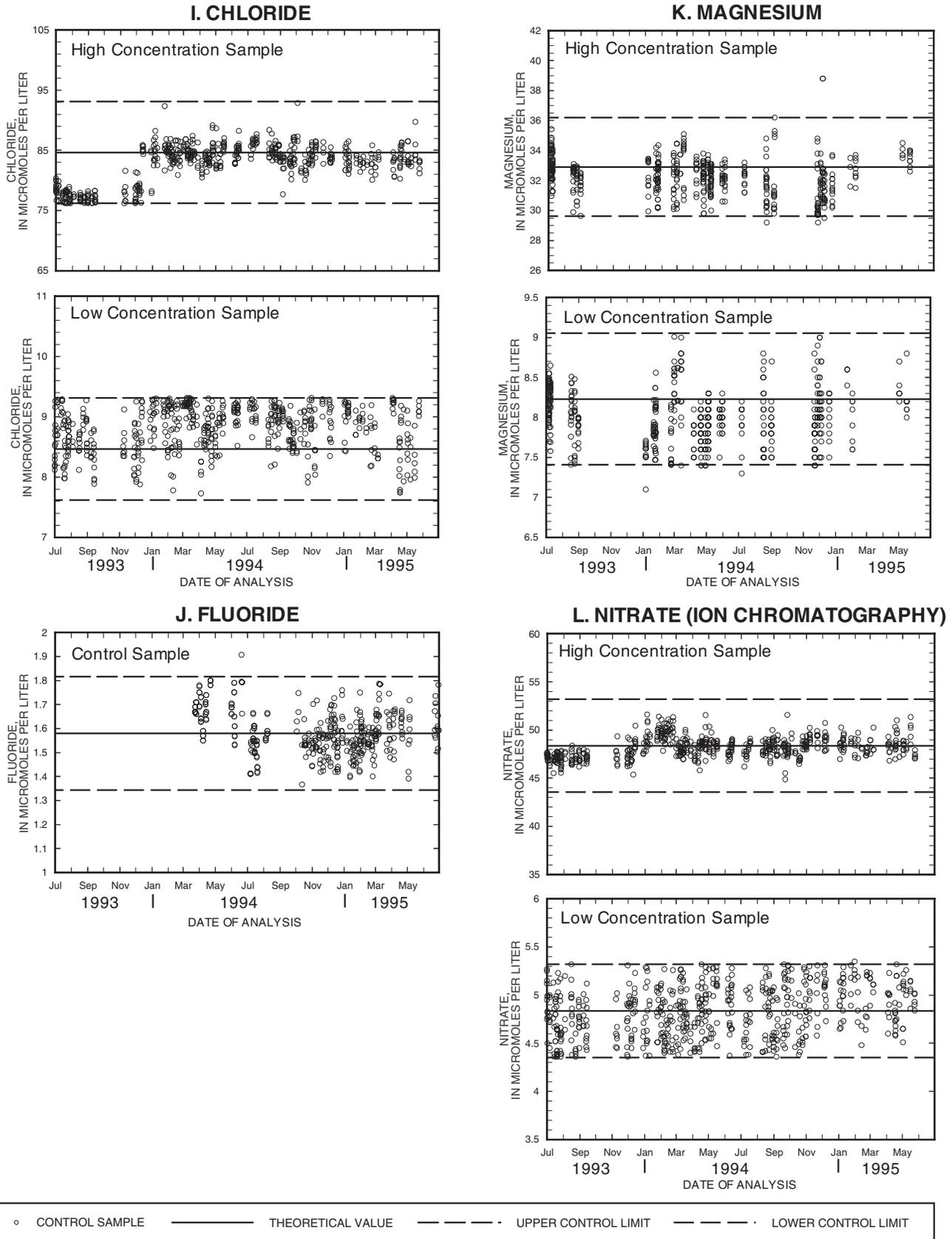
## **Figures 1-5**



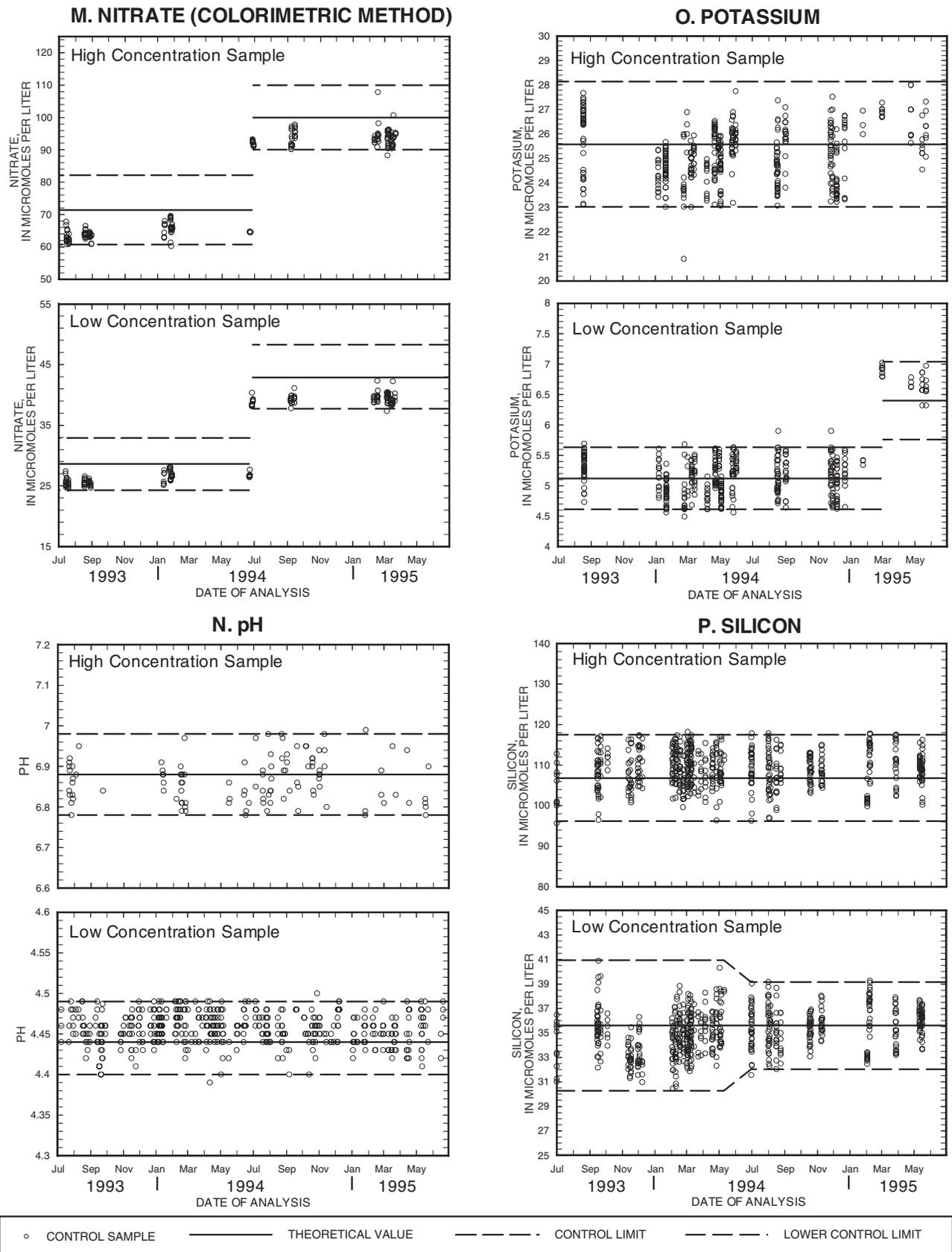
**Figure 1.** High- and low-concentration quality control samples: A. Acid-neutralizing capacity. B. Aluminum, total monomeric. C. Aluminum, total. D. Ammonium.



**Figure 1.** High- and low-concentration quality control samples (continued): E. Calcium. F. Carbon, dissolved inorganic. G. Carbon, dissolved organic. H. Carbon, dissolved organic (soil expulsions).

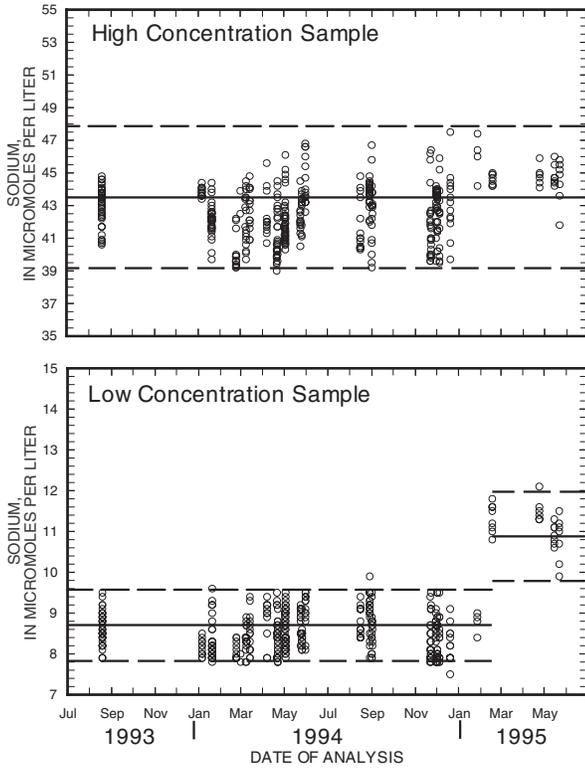


**Figure 1.** High- and low-concentration quality control samples (continued): I. Chloride. J. Fluoride. K. Magnesium. L. Nitrate (ion chromatography).

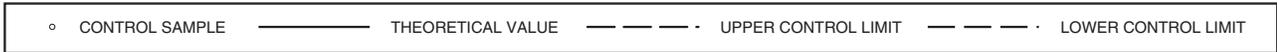
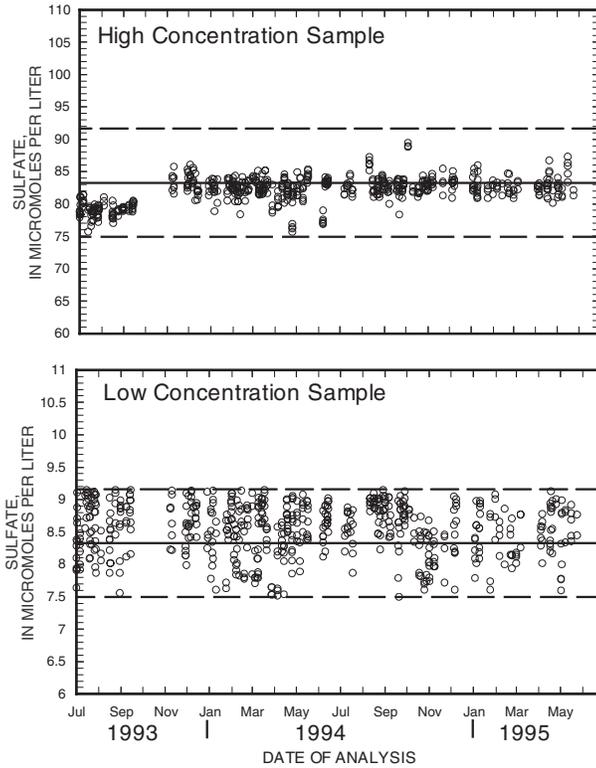


**Figure 1.** High- and low-concentration quality control samples (continued): M. Nitrate (colorimetric method). N. pH. O. Potassium. P. Silicon.

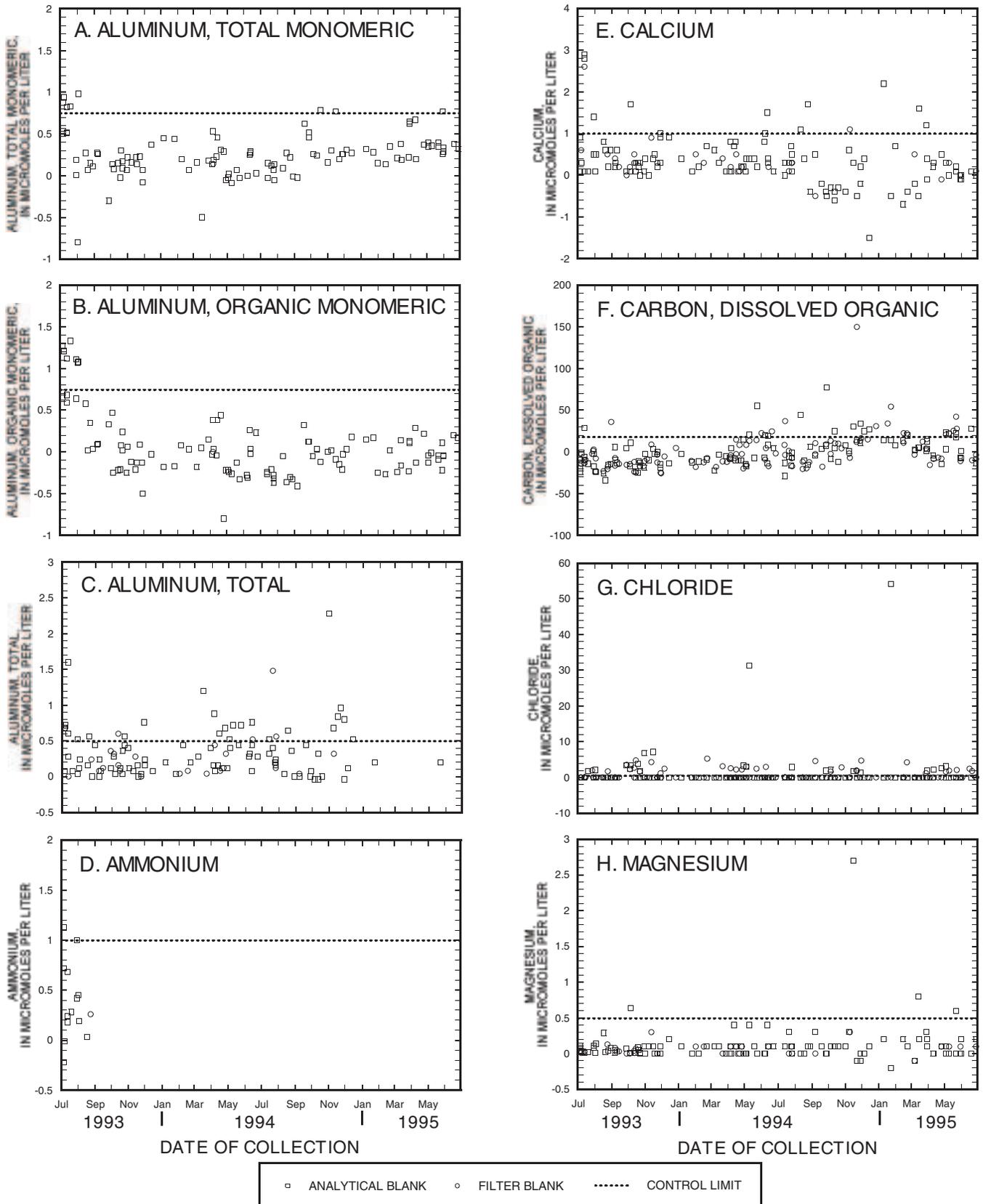
**Q. SODIUM**



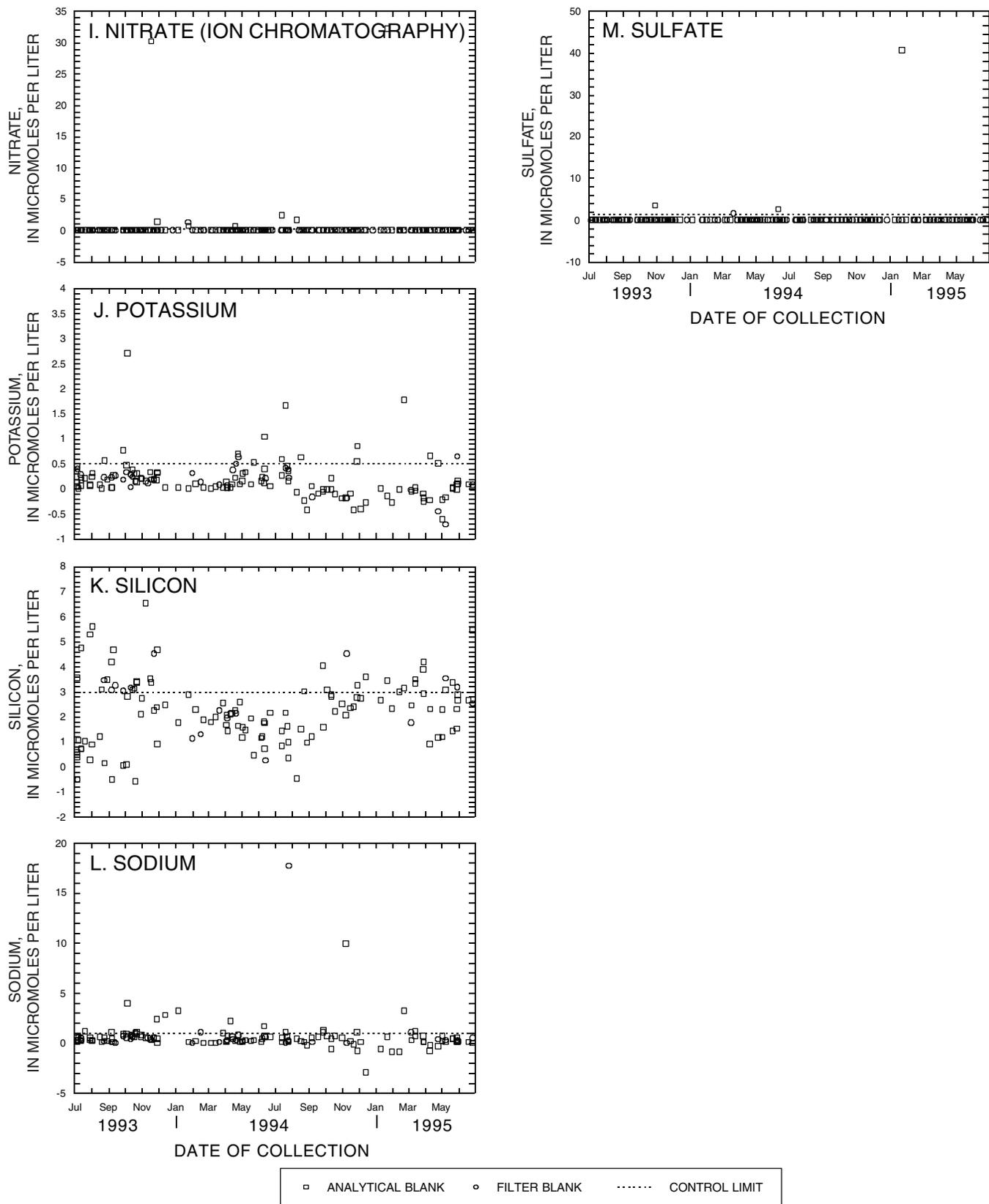
**R. SULFATE**



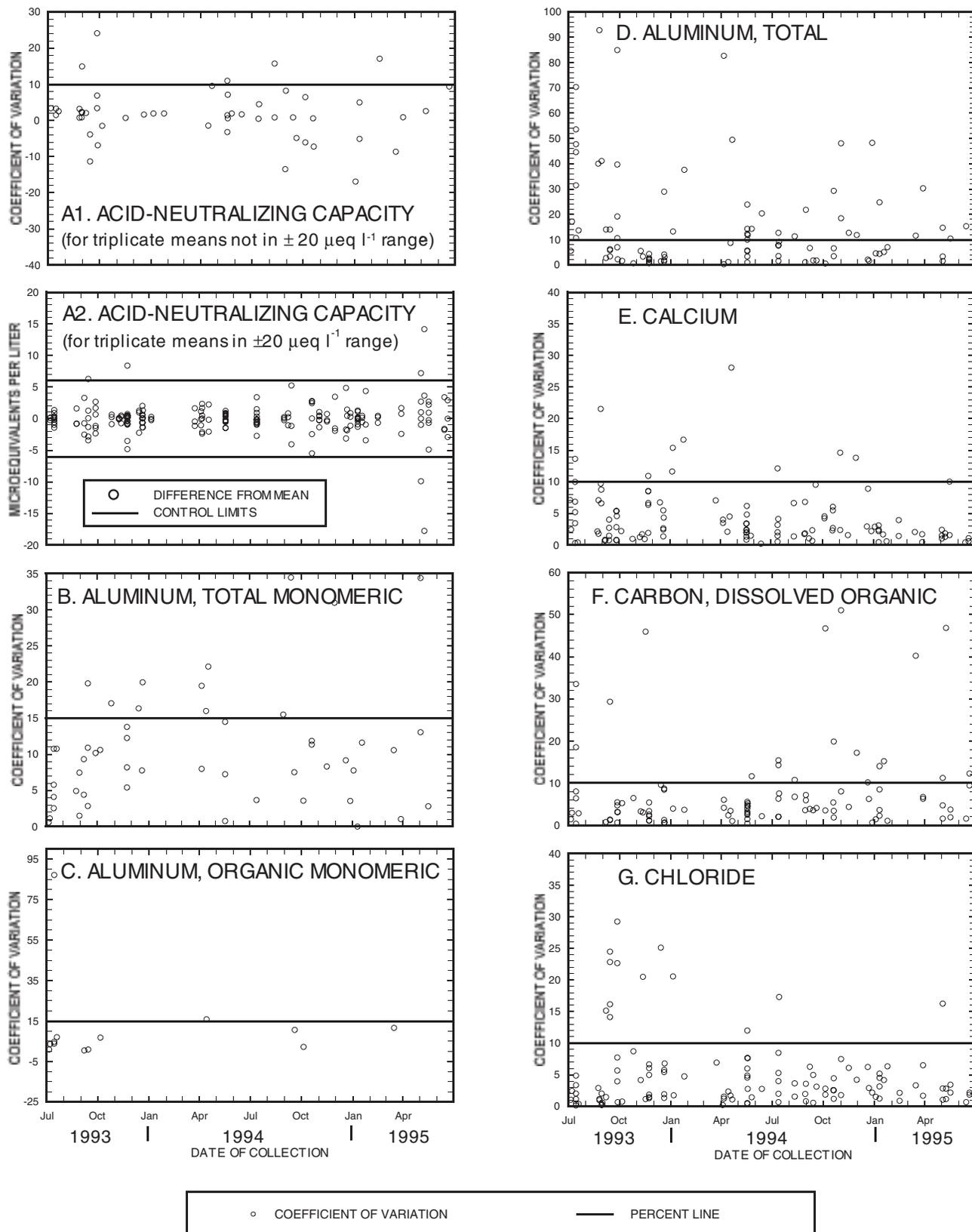
**Figure 1.** High- and low-concentration quality control samples (continued): Q. Sodium. R. Sulfate.



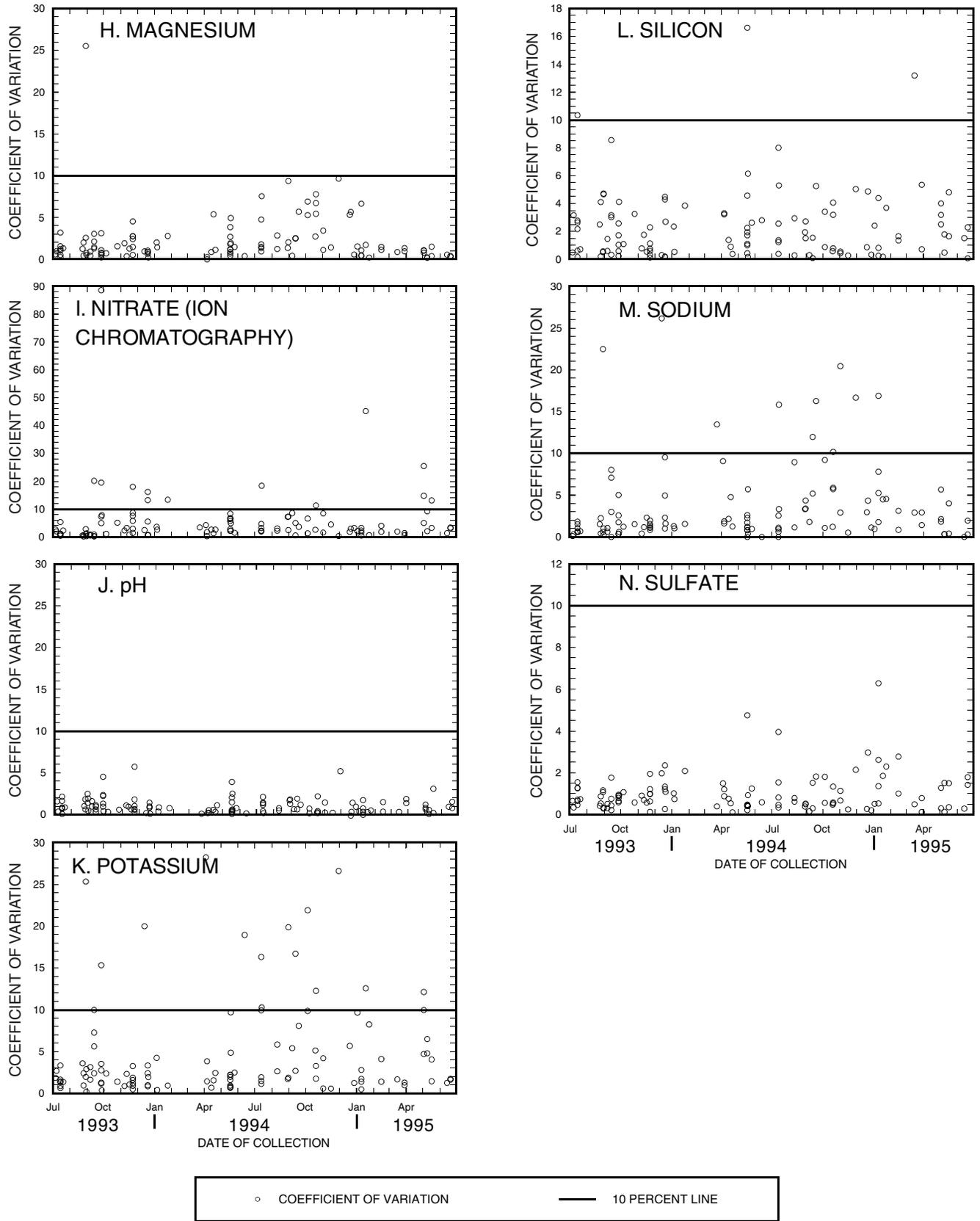
**Figure 2.** Filter-blank and analytical-blank samples: A. Aluminum, total monomeric. B. Aluminum, organic monomeric. C. Aluminum, total. D. Ammonium. E. Calcium. F. Carbon, dissolved organic. G. Chloride. H. Magnesium.



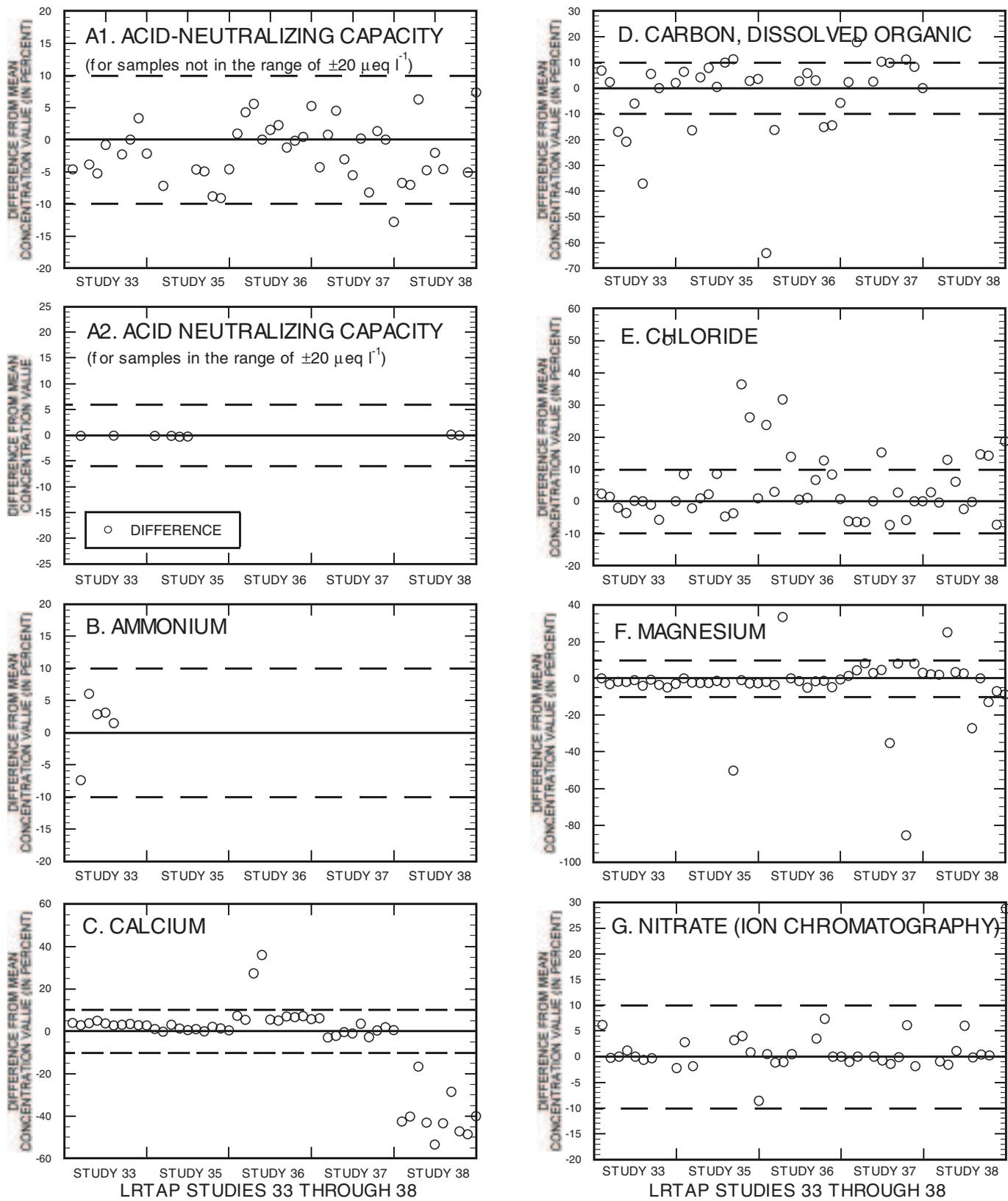
**Figure 2.** Filter-blank and analytical-blank samples (continued): I. Nitrate (ion chromatography). J. Potassium. K. Silicon. L. Sodium. M. Sulfate.



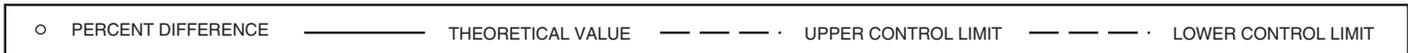
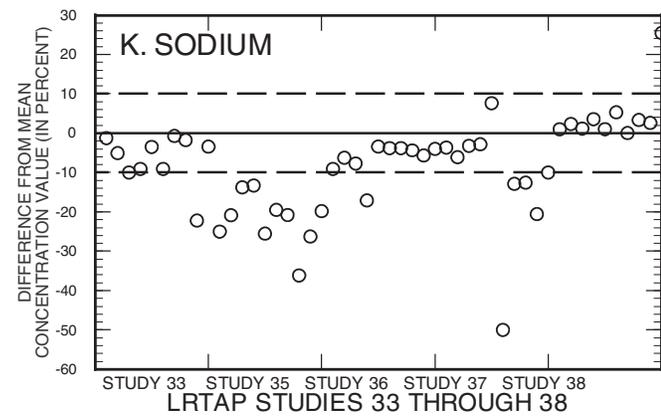
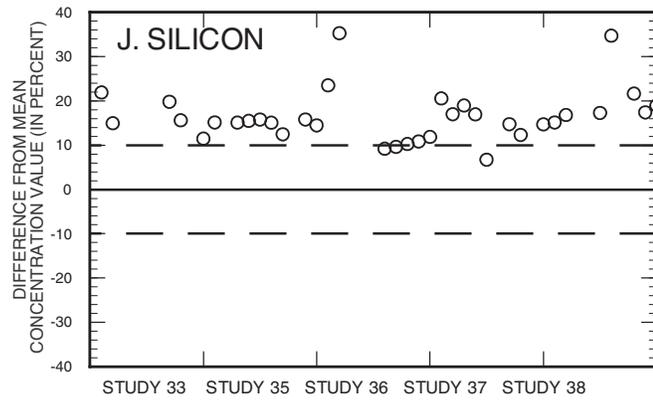
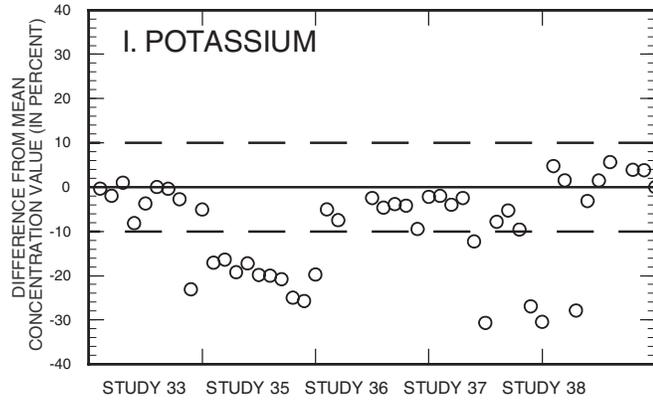
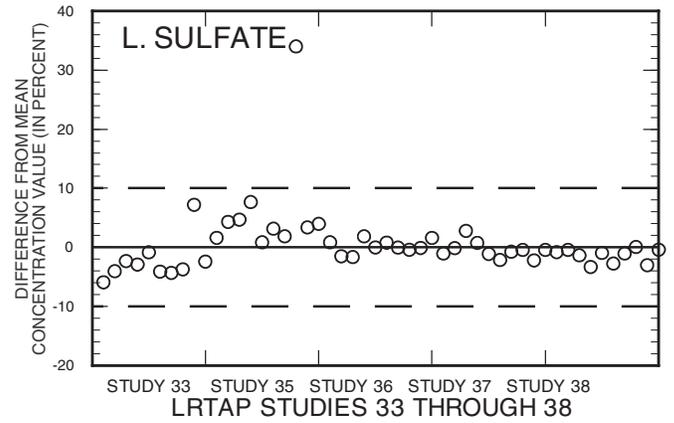
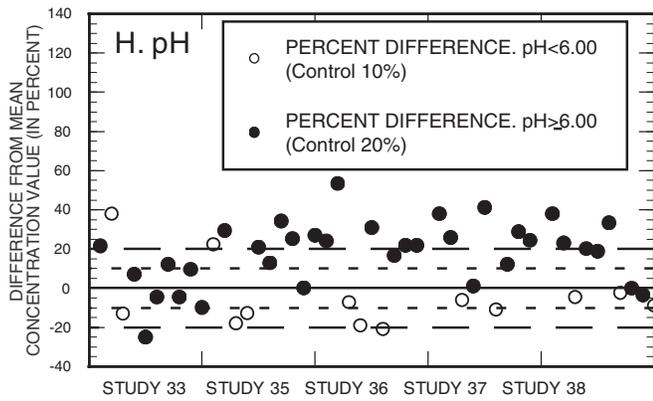
**Figure 3.** Triplicate environmental samples: A1. Acid-neutralizing capacity (for triplicate means not in the range of  $\pm 20 \mu\text{eq l}^{-1}$ ). A2. Acid-neutralizing capacity (for triplicate means in the range of  $\pm 20 \mu\text{eq l}^{-1}$ ). B. Aluminum, total monomeric. C. Aluminum, organic monomeric. D. Aluminum, total. E. Calcium. F. Carbon, dissolved organic. G. Chloride.



**Figure 3.** Triplicate environmental samples (continued): H. Magnesium. I. Nitrate (Ion Chromatography). J. pH. K. Potassium. L. Silicon. M. Sodium. N. Sulfate.



**Figure 4.** Environment Canada, LRTAP laboratory study: A1. Acid-neutralizing capacity (for means not in the range of  $\pm 20 \mu\text{eq l}^{-1}$ ). A2. Acid-neutralizing capacity (for sample means in the range of  $\pm 20 \mu\text{eq l}^{-1}$ ). B. Ammonium. C. Calcium. D. Carbon, dissolved organic. E. Chloride. F. Magnesium. G. Nitrate (ion chromatography).



**Figure 4.** Environment Canada, LRTAP laboratory study (continued): H. pH. I. Potassium. J. Silicon. K. Sodium. L. Sulfate.

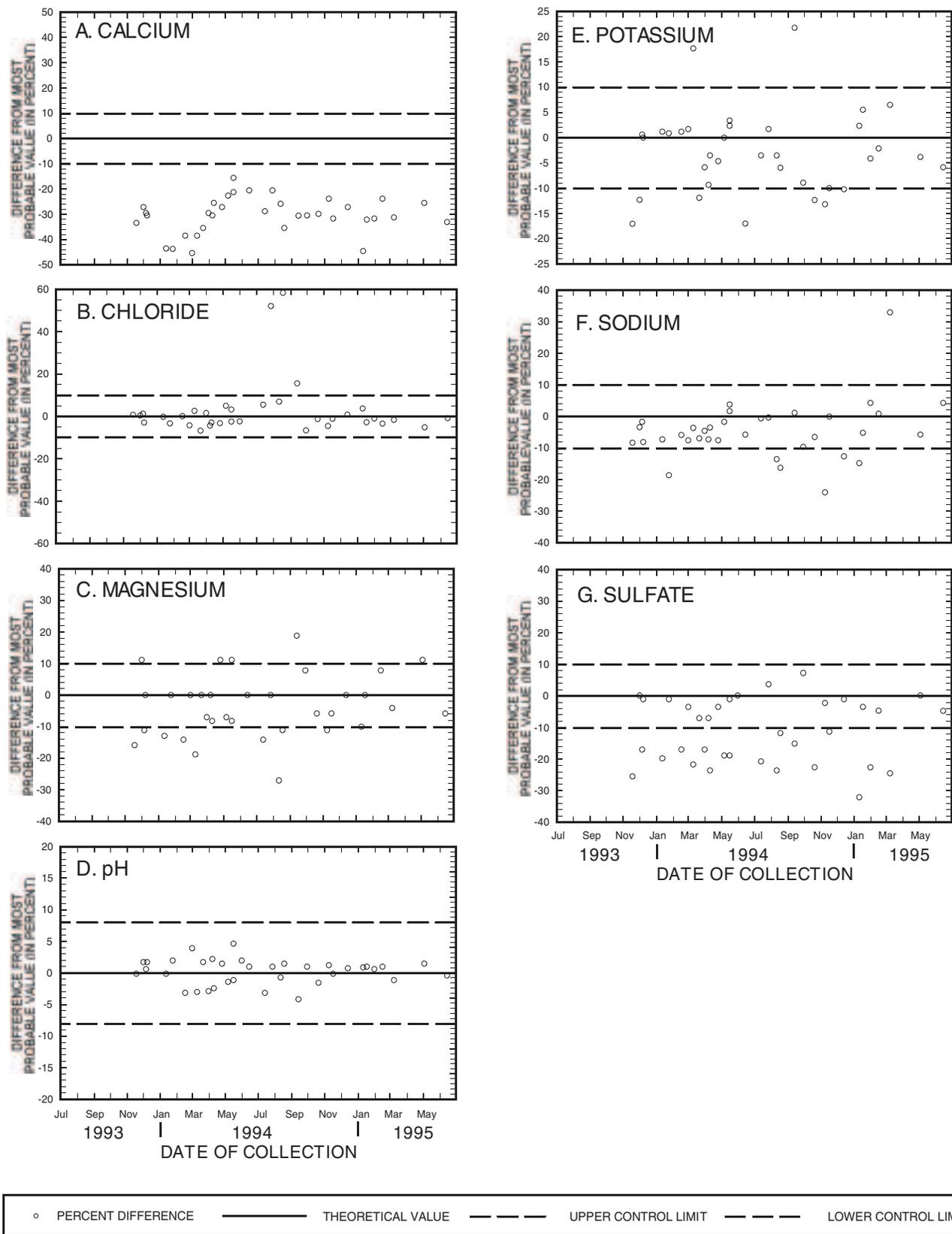


Figure 5. Analytical blind samples: A. Calcium. B. Chloride. C. Magnesium. D. pH. E. Potassium. F. Sodium. G. Sulfate.